12-2005

Paper Substrates for Electronic Printing

Laura K. Wood
Western Michigan University

PAPER SUBSTRATES FOR ELECTRONIC PRINTING

by

Laura K. Wood

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Paper Engineering, Chemical Engineering and Imaging

Western Michigan University
Kalamazoo, Michigan
December 2005

ACKNOWLEDGMENTS

I would like to thank the members of my thesis committee, Dr. Paul D. Fleming, Dr. Margaret Joyce, and Dr. Thomas Joyce, for the time and effort they put forth in advising me these past two years. I would also like to extend my gratitude to all the faculty and staff in the PCI department for making my graduate experience an enjoyable and memorable one.

I would also like to thank my parents, Sam and Joanne, for being so encouraging through my many years of college. Finally, I would like to thank Eastan for being so supportive throughout my Master's career.

Laura K. Wood

PAPER SUBSTRATES FOR ELECTRONIC PRINTING

Laura K. Wood, M.S.

Western Michigan University, 2005

Printed Radio Frequency Identification (RFID) labels utilize conductive inks to provide the means for wireless flow of electronic signals. An RFID label is an identification label with an integrated circuit and antenna that transmits data via radio waves to a reader, which sends the data to a computer for processing. RFID labels allow manufacturers and retailers to accurately track their inventory more efficiently than previously possible with bar codes. However, etched metal RFID labels are too expensive for widespread implementation. The key to reducing the cost of RFID technology is replacing etched metal tags with tags printed with conducting ink.

The present work explores the effects of paper properties on conventional silver-based conducting inks. The effects of smoothness, relative humidity, temperature, porosity, permeability and wetability on electrical properties of silver inks on different paper substrates were studied. It was determined that many of these characteristics do influence the conductivity of a printed sheet. However, the conductivity changes resulting from relative humidity and temperature differences may be attributed to the silver-flake ink, rather than the paper substrate. Further exploration will be required on this topic to achieve the goal of an ideal paper substrate for electronic printing applications.

TABLE OF CONTENTS

ACKNOWLEDGMENTS ii

LIST OF TABLES v

LIST OF FIGURES vi

CHAPTER

I. INTRODUCTION 1

Background of RFID 1

Present Research 2

II. RFID SYSTEM OVERVIEW 3

Components 3

Packaging Issues 5

Classifications 5

Price Considerations 6

Unique Capabilities 7

Privacy and Security Issues 8

III. CONDUCTING INKS 10

Composition 10

Implementation 11

Determining Rheological Properties 12

IV. RFID PRINTING PROCESSES 15

Flexography 15

Lithography 16

V. METHODS 19

Silver-Flake Ink Rheology 19

Substrates........ 19

Ink-Substrate Interactions 20

VI. RESULTS AND DISCUSSION 24

Silver-Flake Ink Rheology 24

Substrates........ 27

Ink-Substrate Interactions 28

VII. CONCLUSIONS........ 34

REFERENCES 34

LIST OF TABLES

1. Description of Sample Substrates 20

2. Mercury Porosimeter Parameters 21

3. Humidity Chamber Parameters 23

4. Conductivity of Silver-Flake Ink on Tested Substrates 28

5. Effect of Surface Roughness on Conductivity 28

6. Parker-Print Porosity and Permeability of Substrates 29

7. Mercury Porosimeter Data for Substrates 29

8. Relationship between Substrate Permeability, Porosity and Conductivity 30

9. Contact Angles of Conducting Ink with Substrates 30

10. Effect of Relative Humidity on Conductivity 31

11. Effect of Temperature on Conductivity 32

12. Effect of Repeated Humidity Change on Conductivity 33

LIST OF FIGURES

1. Silver-Flake Ink Dynamic Stress Sweep 25
2. Silver-Flake Ink Frequency Sweep 26
3. Silver-Flake Ink Steady State Flow 27
4. Relationship between Relative Humidity and Water Content of Air 32

CHAPTER I

INTRODUCTION

Background of RFID

RFID in Industry

Radio frequency identification (RFID) is a technology in which digital data encoded in an RFID tag are automatically transmitted to a reader using radio waves. The reader converts the radio waves back to a digital form and passes the information to computer systems for processing. Invented in 1969 and patented in 1973, RFID was originally utilized in the 1980's to track inventory in harsh environments.[1,2] The employment of RFID tags is rapidly expanding in today's marketplace in a variety of industries, the most prevalent of which is the packaging industry. Also referred to as intelligent packaging, RFID could be used in tracking inventory from cradle to grave. This includes raw materials production, manufacturing and assembly, purchases, deliveries, use, maintenance, and disposal or recycling.[3] Current research in the area is focusing on the use of conductive inks in tag components to reduce the cost of implementation and to make this technology economically viable.

RFID Implementation

The U.S. Department of Defense and retail giant Wal-Mart are leading the way in implementing RFID technology mandates. Wal-Mart is requiring its top one hundred suppliers to include RFID tags on cases and pallets of goods by the end of 2005.[4] Likewise, the Department of Defense is requiring its suppliers to enter contractual relationships agreeing to the utilization of RFID tags this year.[5] RFID labels serve a purpose similar to that of a bar code. These labels consist of an integrated circuit and antenna which provide contact-free transfer of data.[6] The tag's circuit listens for a radio signal sent by a reader. When the tag receives a certain radio signal, it responds by transmitting its unique ID code back to the transceiver.[7] RFID labels offer several distinct advantages over bar codes; the tags do not need line of sight to be read, each item is capable of having a unique serial number, and these tags can be designed in such a way that the information stored on them may be updated or changed.[8]

As their suppliers struggle to keep up with trends, manufacturers are striving to find ways to decrease the cost of the electronic tags.[9] A main goal of printed RFID tags is to provide a low-cost alternative to conventional tags, thereby broadening the potential areas of application. Far less expensive than older-style etched metal tags, printed tags are quickly gaining in popularity. In addition to becoming an economically-viable option, printed RFID components are also more durable than their traditional counterparts. Designed to function even when bent, these lightweight, flexible tags can be subjected to abrasive conditions without failing.[10]

Present Research

The focus of this research is to determine the influence of specific paper properties on a final printed RFID label. The effects of smoothness, relative humidity, temperature, porosity, permeability and wetability are investigated. The information gained from these experiments will be used to engineer an ideal paper grade for use with electronic applications.

CHAPTER II

RFID SYSTEM OVERVIEW

Components

The RFID system is comprised of three basic components: an electronic product code (EPC), an integrated tag, and a reader. The EPC is a new product numbering standard developed by the Uniform Code Council (UCC). Similar to the UPC code used in barcodes, the EPC is used to identify the tagged product. The 96-bit code is transmitted via radio waves from the tag to the receiver.[11] This code, which makes each tag individually identifiable, is divided into several sections. An 8-bit prefix defines the type of EPC, a 28-bit number identifies the product's manufacturer, a 24-bit number describes the type of product, and a 36-bit number assigns the individual product a unique identity. The EPC differs from the UPC in that each tagged item has a unique serial number. This allows companies to differentiate between, as well as track, individual products. The 96-bit tag provides and incredible capacity for information storage. To demonstrate the amount of data an RFID tag can hold, consider the following: 54 bits provides enough storage to number every grain of rice produced in the world, and 138 bits is enough to number every molecule on the surface of the planet. The 96-bit EPC would provide enough storage to support 268 million different companies, each with 16 million product lines comprised of 68 billion individual items.[12]

The tag is comprised of an integrated circuit connected to an antenna. The circuits act as transponders, listening for a radio signal sent by transceivers (readers). The reader controls the system's data acquisition and communication. The reader works by generating an excitation field that powers the tag. The reader decodes the data signal and formats it for sending to a host computer for further processing. When the transponder receives a signal, it responds by transmitting its unique ID code (its EPC) back to the transceiver.[8] The reader then feeds this code to a computer and a piece of software looks up the EPC, using a network connection, in a database, which locates an Internet address where the product information is stored.[12] The antennae are the conduits between the circuit and the transceiver, emitting radio signals to activate the tag and read and write data to it. Traditionally, the antenna had been constructed from an etched metal, typically copper or aluminum, to generate electricity. Older RFID systems used inductance to transfer information. Some tags even had their own batteries.[13] Though effective, this was a costly tracking technique.

Today, industries are beginning to employ tags printed with conductive ink antennae as a more cost-effective alternative. The antennae are printed directly on a substrate using silver-, carbon- or silver/carbon-based inks.[14] Since radio waves travel through most packaging materials, packagers will have a lot of flexibility in how they print the antenna. For example, the antenna could be printed inside the box, laminated inside the package, printed outside the box, or it could be printed over.[15] The tags are powered by the radio signal that "wakes them up" and requests a response.[6] Placement of the antenna on the package is important to the resulting signal strength. For the reader to work correctly, the antenna must be oriented in such a way as to prevent RFID labels from overlapping and shielding each other out. One industry goal is to eventually produce boxes containing built-in RFID labels so that end users will not have to place the tags themselves. This would save some time in the packaging process and make the technology easier for the users to implement into their systems.[16] The antenna size and shape also influences the resulting frequency. Global radio regulations define specific frequency use for specific countries. The frequencies of greatest interest to RFID are 865 MHz in Europe, 915 MHz in the U.S., and 950 MHz in Japan. RFID antennae frequencies are tuned according to the properties of the labeled materials, as well as the substrates they are printed on. Frequency is also affected by antenna length. Bigger antennas generally produce a longer read-range. All of the above factors must be considered while designing and placing an RFID antenna to produce optimum performance.[17]

Packaging Issues

Another challenge presented by this technology is the effect the package contents could have on the signal strength. Since liquids block electromagnetic fields at high frequencies, their effect on reading capabilities must be taken into account. A lower operational frequency could be employed, but since the industry is focused on using high-frequency RFID tags, packaging designs that would allow the use of high frequency tags on liquid shipments are being researched.[16] Packaging metallic products has also proven problematic. Since metal reflects radio waves, an RFID tag placed directly on metal will not read correctly.[17] One packaging solution that has been presented suggests that pallets with liquid-containing packages put gaps between layers of cases. This may allow electromagnetic fields to penetrate through the pallet.[16]

Classifications

RFID tags can be classified as active or passive. They range in capabilities from simple tracking devices to encryption and read/write ability. The operating power for passive tags is supplied by the reader, so they are less complex than active tags. These small, lightweight and cheap tags can have a lifetime of ten years or more. The downside of passive tags is that their range of transmission is shorter, so the readers used for RFID systems must be high-powered. On the other hand, active RFID tags can transmit data over longer ranges and require less power from the readers. Currently, most active tags are powered by a battery with a lifespan of two to seven years. Not surprisingly, active tags are more expensive and larger than passive tags. The more capabilities the RFID tag has, the bigger the tag needs to be.[18] Unlike bar codes, both passive and active tags are capable of being reprogrammed with new information.[8]

Tags can be further classified as read-only (R/O) tags or read-write (R/W) tags. R/O tags are fixed with a set, tamper-proof, unique identification code. This code is known as a license plate, and enables the tag to be cross-referenced with a computer database. This allows the user to track the tagged item along each step of its lifecycle. R/W tags can be either R/W Once tags or R/W Many tags. R/W Once tags can be field programmed. This means that the data stored in the tag can be entered even after the tag is affixed to the product. This capability proves to be an advantage by allowing the user greater flexibility in the application process. Once the information is written to an R/W Once tag, the tag acts like an R/O tag. R/W Many tags, however, may be rewritten with new information whenever needed. This is advantageous in instances where the identification code must be changed, such as in a reusable container. This is also important where variable data are preferred over a unique identity.[18]

Price Considerations

To date, the main disadvantage of RFID tags have been cost. Tags were initially as much as $200 each. They fell to $1 in 2000, and they plummeted in recent years to 25 – 50 cents. However, to be cost effective, tags should be a nickel or less at pallet or case level, and a penny at individual level. The industry is turning towards print technology to help break the current 10 cent/tag barrier and further reduce cost. Experts insist that an antenna that costs a penny or two is possible in the near future.[15] Tag readers have been known to cost a couple thousand of dollars each. The costs of the readers have fallen in recent years as well; a realistic target price for these tag readers is $100.[12]

Unique Capabilities

RFID systems offer numerous benefits over more traditional product tracking systems. One such benefit is the protection RFID offers against product counterfeiting. Product counterfeiting is a $500 billion problem across the globe, primarily in the area of pharmaceuticals. When counterfeit pharmaceuticals are discovered, the entire stock accompanying it must be discarded. This accounts for a sizable loss in the pharmaceutical industry. Though counterfeiters may be able to duplicate authentic product packaging, they are far less likely to be able to reproduce a uniquely identified RFID tag.[19] Another area of potential gain lies in increased speed and productivity. Industry experts report that distribution productivity can be increased by as much as 10 to 20 percent with RFID systems. Furthermore, inventory accuracy can surpass the current 90 percent acceptance rate, approaching the ideal 100 percent mark.[20] In 2003, Delta Air Lines Inc. conducted a test using RFID tags to track 40,000 pieces of luggage from check-in to plane loading. Delta reported accuracy levels ranging from 96.7% to 99.9%, illustrating the success of the RFID process.[21] Finally, retail store productivity can be improved by 5 percent at the case level and 7 percent at item level, allowing store labor to be redirected to customer-facing initiatives.[20] Much of the increase in speed can be attributed to the fact that EPC codes do not need line of sight to be read. Locating and scanning codes on individual cases can average four to five seconds per case. With RFID, retailers are instead able to place cases on a high-speed conveyor that will pass by a reader where the electronic code is transmitted. The labor savings during tracking processes will amount to multi-million dollar cost reductions for businesses.[22] RFID can allow retailers to go a step further and track inventory as it is placed and removed from store shelves. The system will automatically update the inventory data and could order more product as needed. This concept will cause out-of-stock items to become a problem of the past. RFID implementation stands to greatly reduce costs by fostering faster, more detailed inventory control.[23]

RFID technology can be used to accomplish tasks that would not otherwise be possible. Smart labels can allow retailers to monitor product conditions and locations at any point in the supply chain. For example, they can be used to ensure that perishable goods, such as foods and pharmaceuticals, are shipped and stored at an appropriate temperature. This could eliminate unnecessary waste due to spoiling or contamination and ensure the quality of the product. An RFID label using a conductive ink antenna, a chip and a sensor can potentially alert a supplier to damaging shifts in temperature.[24,23]

Privacy and Security Issues

RFID technology has been met by some with trepidation due to security concerns. Traditionally, information encoded in smart tags has been protected against tampering or theft using encryption and with some write-once only “locks”.

These methods will continue to be used in closed-environment applications. The issue becomes more complicated in an open-environment application, which means packages traveling between two or more companies. In many cases, packages need to be read by a manufacturer, a distributor and a retailer. This makes encryption difficult, because the product must be identifiable during every step of its lifecycle. At the same time, the code must be protected against outside intervention.[25] This is especially pertinent with passive RFID tags, where the power source comes from the receiver, not from a battery within the RFID tag itself. Once the tag is in proximity of a tag reader, it will continue to broadcast the ID information to anybody possessing the capability to receive it. To prevent unique identifiers from being duplicated, sufficient encryption must be available. Some consumers also worry that RFID technology would let third parties track their shopping habits more closely than they already do.[26]

CHAPTER III

CONDUCTING INKS

Composition

Conductive inks typically consist of finely dispersed conductive particles in a resin system.[24] More rarely, they can be composed of conductive polymers.[23] These inks can be used to create patterns on both flexible and rigid substrates. The conductive particles present are typically carbon or silver, or a mixture of the two. The ink composition is chosen based on the purpose of the end product. Silver inks provide long read ranges for circuit designs and RFID antennae, which is why they are often implemented in these applications. Carbon inks are typically used for low-power products, including the anti-static treatment used to protect electronics, and in cases where only short RFID read ranges are required.[24] Though etched copper and aluminum antennae offer the lowest resistance, printing with conductive silver ink is the most cost-effective option. It also gives an acceptable signal of 900 MHz.[17]

Conductive inks are designed to allow the wireless flow of electricity. The inks are capable of serving the same purpose as wires, resistors or antennas. Conductive inks have been most commonly used in circuit boards where etched copper circuits were unfavorable, such as membrane switches and printed wiring boards.[23,24] More recently, conductive inks have served as antennas for RFID tags. Currently, companies are focusing on implementing the use of high-speed printing processes to manufacture RFID antennas.[23]

Conductive inks offer several distinct benefits: they are generally less expensive than etched metal for traditional electronic circuits, contain few volatile organic compounds (VOCs) and are compatible with numerous substrates. Traditional etched metal electronic circuits require a 10-step manufacturing process that demands high capital investment and generates hazardous acid wastes. On the other hand, conducting inks have relatively low VOCs and are considered to be much more environmentally friendly than their more traditional counterparts.[24]

Implementation

Flint Ink, headquartered in Ann Arbor, MI, established a new business unit, Precisia LLC, in August of 2003 to develop conducting ink technology.[23] Conducting inks are more expensive than ordinary commercial inks, due to their metallic content. However, by keeping the printed layer relatively thin and designing an antenna small in size, the printed antenna can be kept inexpensive. Even using expensive ink, printed antennae are much more affordable than their etched metal counterparts. Precisia's inks include particles of silver, chosen because, unlike copper, they still offer the required conductive properties after oxidizing.[15] Precisia is researching the performance of inks in place of etched metal antennae at various frequency bands used in the RFID process. They have determined that the ink antennae compare well to copper at ultra-high (860 MHz to 950 MHz) and microwave (2450 MHz) frequencies. An extra step, like elevating temperature or electroplating, can be performed at high frequency (13.56 MHz) to enhance ink antennae performance, so they work as well as coil antennae.[23]

Conducting inks are being used to produce RFID antennae using flexographic, rotogravure and lithographic printing techniques. The flexographic and gravure inks are water-based, whereas the lithographic inks are oil-based. Precisia has determined that line resolutions of 50 microns are possible with the flexographic and gravure inks, and line resolutions of 40 microns are achievable with the lithographic inks. These line resolutions are sufficient to produce compact and complex circuit designs. The conducting inks possess a sheet resistance of up to 100 milli-ohms/square at a film thickness of approximately 8 microns. Ink formulations can be adjusted to cover a wide range of sheet resistance at a film thickness of 2 microns or less for printed resistors.[24]

Determining Rheological Properties

A dynamic stress rheometer is used to examine the quantitative parameters of a viscoelastic fluid. Unlike a viscometer, a rheometer measures both the viscous and elastic contributions to viscosity. The rheometer conducts steady shear (stress, strain and time/temperature sweeps) and dynamic oscillation (frequency, stress/strain, and time/temperature) experiments.

A dynamic stress rheometer uses an air bearing and motor assembly to control the spindle. The air bearing is important, because it controls the rotation of the spindle assembly without contacting it. This non-contact assembly insures that no additional shear is placed upon the spindle. The spindle contacts only the fluid being measured. The rheometer is also capable of accurate temperature control of the sample.

The stress is calculated from the torque in a rheometer. Torque is a measure of how much force acting on an object causes that object to rotate. In the case of the rheometer, the force needed to cause the spindle to rotate in the fluid is used to calculate the torque. The torque range is fixed and defined by the instrument's specifications. The angular displacement is related to the shear strain and is measured by an optical encoder. The angular velocity is directly related to the shear rate. The stress range can be varied by changing the geometric configuration of the machine. Several geometries exist. Among these are concentric cylinders, cone and plate, parallel plate, and torsion rectangular. The proper geometry is selected according to the viscosity of the material.[27]

The rheological properties of an ink determine how the ink will behave in a variety of process situations. A material's rheological properties can be examined by executing an oscillation experiment on a rheometer. In an oscillation experiment, deformation is applied sinusoidally using a defined stress amplitude and frequency. Both the viscous and elastic contributions to the material's viscosity can be determined from the resulting output. The viscous modulus (loss modulus) measures the material's ability to dissipate energy, while the elastic modulus (storage modulus) measures the material's ability to store energy.

During a stress sweep, the sample is subjected to an increasing stress while constant frequency and temperature are maintained. A frequency of 1 Hz or 10 Hz is typically used. The sample's response to the stress is displayed and the linear viscoelastic region is determined. The elastic modulus (G') and the viscous modulus (G") are plotted against stress. The elastic (storage) modulus is a measure of the elastic contribution to the overall viscosity. This is also the ability of the material to store energy. The viscous (loss) modulus is a measure of the viscous contribution to the overall viscosity. This is also the ability of the material to dissipate energy. Tan delta is a measurement of material damping. Delta is the phase angle. This is the measured shift between the input wave and the output wave in an oscillation experiment. A perfectly viscous material exhibits a phase angle of zero, while a perfectly elastic material exhibits a phase angle of ninety degrees. Tan delta is equal to elasticity divided by viscosity. The linear viscoelastic region (LVR) is the stress range in which the G' and G" values are linearly related before they drop off due to deformation. The LVR can be determined during a stress sweep at a constant frequency and temperature. G' and G" are plotted against stress. The region where both G' and G" are linear, before they drop off due to deformation, is the LVR. Determining the LVR is important, because a frequency sweep needs to be conducted at a stress within the LVR to give useful data. The LVR also reveals the critical stress value. This is the stress at which deformation begins to lower G' and G" values. When the sample is subjected to a stress within the LVR, the material will be able to recover from the deformation it undergoes. Outside of the LVR, the deformation cannot be completely reversed.

In a frequency sweep, the frequency is varied while constant stress and temperature are maintained. The frequency sweep is run at a stress value within the linear viscoelastic region, determined during the previous stress sweep. Frequency is a measure of the time needed to complete one oscillation and is defined as the inverse of time. The frequency sweep is used to determine the time dependency of the sample's deformation. The frequency sweep reveals the time dependency of the material in respect to deformation. It also provides the gel strength. Here, the slope of the G' curve is used to determine the material's strength. A large slope reveals low strength, and a small slope indicates high strength.[28]

CHAPTER IV

RFID PRINTING PROCESSES

Flexography

Flexographic printing, or flexography, is a rotary relief printing process first introduced in the early 1900s. Originally called aniline printing due to the aniline dyes the inks were comprised of, flexography uses a flexible plate with raised image areas.[29] The flexible plate is manufactured from rubber or photopolymer material and attached to a rotating cylinder.[30] Flexographic inks are quick-drying and have a low viscosity. The inks are designed to lie on the surface of nonabsorbent substrates and solidify when solvents are removed.[31] The combination of a flexible plate, fast drying ink, and the ability to print on such a wide variety of substrates makes this a popular choice for package printing.[28] The four main unit operations in flexography are image preparation, platemaking, printing and finishing.[29]

Flexography is directly related to the oldest printing process, letterpress, in that both technologies employ the use of a relief type plate. A relief plate has raised images; this is the only part of the plate that comes in contact with the substrate during printing.[29] Originally, letterpress arranged individual raised metal characters (types) into words and sentences to form the desired image. The characters were covered with ink and pressed against paper in a mechanical press. In relief printing, only the raised image touches the ink. These raised images are called image areas; the recessed part of the plate is called the nonimage are. Nonimage areas do not receive any ink and do not come in contact with the substrate being printed.[28]

Unlike the letterpress process, which printed using a flat surface, flexographic plates are made of a flexible material. This allows the plate to be attached to a cylinder for ink application.[29] The printing press evolved from using a flat surface to a cylindrical one in order to speed up the process.[28] Flexographic plates may be manufactured from materials such as plastic, rubber or UV sensitive polymer (photopolymer). The three primary methods of making flexographic plates are photomechanical, photochemical and laser engraving.[29]

There are five types of printing presses employed for flexography: the stack type, central impression cylinder (CIC), in-line, newspaper unit, and dedicated 4-, 5-, or 6-color unit commercial publication presses. Each type consists of the same basic units. They include a plate cylinder, an anilox roll (applies ink to the image area), and an ink pan. During the printing sequence, an image is printed as the substrate passes through several print stations. Various tones and colors are created by applying a single color at each station. Magenta, cyan, yellow and black inks are the four basic process colors employed.[29]

Lithography

Lithographic printing, also called lithography, was developed by Aloys Senefelder over 200 years ago. The original process required that a slab of stone (such as limestone) be ground down to a perfectly flat surface; this process was called graining. Next, the printer would draw on the surface with a grease crayon to form a printing image. A gum arabic solution (an etch) would then be worked into the stone surface. During this etching process, the gum absorbs into the non-image areas of the stone and solidifies the image areas. The non-image areas will accept water, whereas the greased image will not. Water is applied to the plate and the plate is inked for printing. The greasy image area will accept the ink and the wet non-image area will not. The plate is then pressed against the paper to transfer the image to the sheet.[27]

Modern lithographic processes are likely to use thin aluminum plates in place of lithographic stones. However, the same basic principle is applied. Lithography, as currently employed commercially, is referred to as an offset printing process. This means that the ink is not directly applied from the plate to the final substrate. Instead, the ink is applied to the plate to form an image and is then transferred to a rubber "blanket". Finally, the image is transferred from the blanket to the final printed substrate.[29] This is done to eliminate the need to create a reverse-reading image on the original plate, as required in the stone lithography process. A right-reading image can now be created on the aluminum plate and the rubber blanket serves as an intermediary between the plate and the substrate, so that the final image is also right-reading.[27]

Lithographic plates are categorized as either negative working or positive working. Negative working plates are exposed through photographic negatives, whereas positive working plates are exposed through photographic positives. Additionally, presensitized plates can be additive or subtractive. Additive plates have a wear-resistant lacquer or pigmented resin added to the image area, and subtractive plates are coated with an oil-attracting resin. A developer removes the oleophilic resin coating from the non-image area, and the plate is left with an oil-accepting image area.[32]

The aluminum plates form a layer of aluminum oxide on their surface which can be anodized for reinforcement. A gum is added to the dampening solution to increase the water receptivity of the plate surface. Often, gum arabic (a polysaccharide with ether linkages, hydroxyl groups and carboxylic acid groups) is used. The gum works because the carboxyl groups react with the aluminum oxide surface to attach itself to the plate. The oxygen molecules in the ether and alcohol groups hydrogen bond with water to wet the plate's surface. The dampening solution has a low pH (to allow carboxyl groups to attach to the plate) and contains additives to increase its performance. A buffer is present to prevent corrosion of the plate, an alcohol works as a wetting agent and reduces surface tension to prevent emulsification of the ink into the dampening solution.

CHAPTER V

METHODS

Silver-Flake Ink Rheology

A water-based flexographic conducting ink (Precisia[33]) comprised of silver flakes was applied to five label-stock substrates. The influences of various substrate properties on the printed conductivity were examined. The rheological properties of a conducting silver-flake ink were studied prior to application. A dynamic stress sweep was conducted on the material to determine its linear viscoelastic region (LVR), as well as the behaviors of the elastic modulus and the storage modulus. A frequency sweep was conducted to observe the time-dependency of the ink. Finally, a steady state stress sweep was completed to determine how the viscosity of the sample changed with increasing stress levels.

Upon viewing the sample's apparent viscosity, the couette geometry was chosen. The couette is appropriate for low viscosity samples and is capable of a high shear rate. After installing the geometry and loading the sample, a conditioning step was performed to pre-shear the substance. The dynamic stress sweep was executed in a range from 0.001809 Pa to 100 Pa at a frequency of 1Hz and 25°C. The frequency sweep was performed on the sample at the predetermined stress of 0.1 Pa. The sweep ranged from 1 Hz to 100 Hz.

Substrates

Five substrate samples were provided by Stora Enso for analysis in conjunction with conducting silver-flake ink. These substrates are listed below in

Table 1 along with their intended applications. The substrates are label-stock grades, appropriate for RFID.

Grade	Description
LabelSet SP	Wet strength labels for beverage bottles
OptiTherm	Direct thermal tickets and tags
PointFlex	Flexible packaging
UniTherm	Pressure-sensitive thermal transfer applications with conventional pre-print applications
UniTherm Sharp	Pressure-sensitive thermal transfer applications with demanding conventional pre-print requirements

Table 1: Description of Sample Substrates

Each substrate was characterized in terms of its roughness, porosity (Parker Print Surf Tester, Mercury Porosimetry), and wetability (contact angle - First Ten Angstroms Dynamic Contact Angle Tensiometer). In addition, the permeability of each substrate was calculated from its Parker Print porosity value and its thickness using the following equation: [34,35]

$$K = 0.048838 * Q * X \qquad (1)$$

Where K is the permeability in μm^2, Q is the flow rate in ml/min and X is the thickness in m.

Ink-Substrate Interactions

Conductivity

The silver-flake ink was drawn down on the substrate using a flexographic "hand-proofer"[36] and the conductivity of each sample was then determined using a Keithley multimeter model 2400. Two flat alligator clips were placed 20 mm apart on the inked area and a voltage range of -0.1V to 0.1V was passed between the probes.

Conductivity was calculated from the I-V curves using the following equation:

$$\sigma = \frac{L \times I}{V \times A} \qquad (2)$$

Where L is the length of the gap, I is electric current, V is applied potential difference and A is the cross-sectional area of the sample calculated as thickness × width of the sample.

Porosity

Each substrate was analyzed in the AutoPore IV Mercury Porosimeter (Table 2). Porosimetry is the measurement of the porosity-related characteristics of a material. These characteristics include pore size, volume, distribution and density.

Operational Parameters	
Penetrometer: #s/n – (13) 3 Bulb, 0.412 Stem, Solid	
Hg Parameters	
Adv. Contact Angle: 130 degrees	Rec. Contact Angle: 130 degrees
Hg Surface Tension:485 dynes/cm	Hg Density: 13.5335 g/mL
Low Pressure	
Evacuation Pressure	50 μmHg
Evacuation Time	5 mins
Mercury Filling Pressure	0.48 psia
Equilibrium Time	0 secs
Maximum Intrusion Vol.	100.000 mL/g
High Pressure	
Equilibrium Time	0 secs
Maximum Intrusion Vol.	100.000 mL/g

Table 2: Mercury Porosimeter Parameters

The mercury porosimeter characterizes the porosity of a material by applying varying levels of pressure to a sample immersed in mercury. The pressure required to intrude mercury into the sample's pores is inversely proportional to the size of the pores. The pressure versus intrusion data is collected by the instrument, and volume and size distributions are generated using the Washburn equation.[37]

Wetability

The contact angle of the silver-flake ink with each substrate was determined using the First Ten Angstroms Dynamic Contact Angle Tensiometer. The tensiometer works by dispensing a single drop of a chosen liquid from a syringe onto a strip of the sample substrate. The camera takes a picture of this sessile drop and the image is analyzed by computer software. A low contact angle indicates high wetability and a high contact angle indicates a low wetability.

Roughness

UniTherm Sharp was calendered to four roughness levels and hand-proofed with silver flake ink. UniTherm Sharp was chosen for this procedure because it had the highest initial roughness value of the five substrates. Conductivity measurements were taken to determine the effect of roughness on the final printed product. Parker Print-Surf roughness[38] values were determined at a clamping pressure of 1000 kPa with a soft backing.

Relative Humidity and Temperature

OptiTherm samples hand-proofed with silver-flake ink were conditioned at various relative humidity and temperatures. Relative humidity is defined as the ratio p_w/p_{ws} where p_w and p_{ws} are the vapor pressure and saturated vapor pressure at the appropriate temperature.[14] The conductivity of each sample was determined to explore the effect of relative humidity on a final printed product. A CARON 6030

Environmental Test Chamber was used to condition the samples to the desired temperature and humidity levels. The operating parameters of the humidity chamber are displayed in Table 3.

CARON Model 6030 Specifications	
Temperature Range without lights	5°C to 60°C
Temperature Range with lights	10°C to 60°C
Heater	1160 Watts @ 115VAC
Compressor	1/4hp, 2940 BTU/Hr@7°C Evaporator
Temperature Control	± 0.1°C
Temperature Uniformity	± 0.3°C
Relative Humidity	20 to 98% RH
Humidity Control	± 2%
Electrical	115V/25A/60Hz 1Ph.

Table 3: Humidity Chamber Parameters

In several measurements, the sample was removed from the chamber and exposed to ambient conditions after the conductivity was determined at the desired humidity level. Three subsequent measurements were taken (Open 1, Open 2, and Open 3) to observe the effect the sudden change in relative humidity had on conductivity of the printed sample.

CHAPTER VI

RESULTS AND DISCUSSION

Silver-Flake Ink Rheology

The dynamic stress sweep performed on the conducting ink is pictured below in Figure 1. Within the LVR, the G' (storage modulus) values were greater than the G" (loss modulus) values, indicating that the sample performed more elastic than viscous. A stress of 0.1 Pa was chosen for the frequency sweep. A crossover point, in which the paths of G' and G" crossed, was observed around the stress value of 1 Pa. This crossover point corresponds to the point in steady flow in which the viscosity drops. After the initial drop of G' and G" outside of the LVR, a second stability plateau can be seen before G' and G" decrease further. The first drop may be attributed to the deformation of the structure created by the silver flakes. Likely, the second plateau is due to the structure of the remaining polymers present in the water-based ink. The second drop would be due to the destruction of the order of these particles.

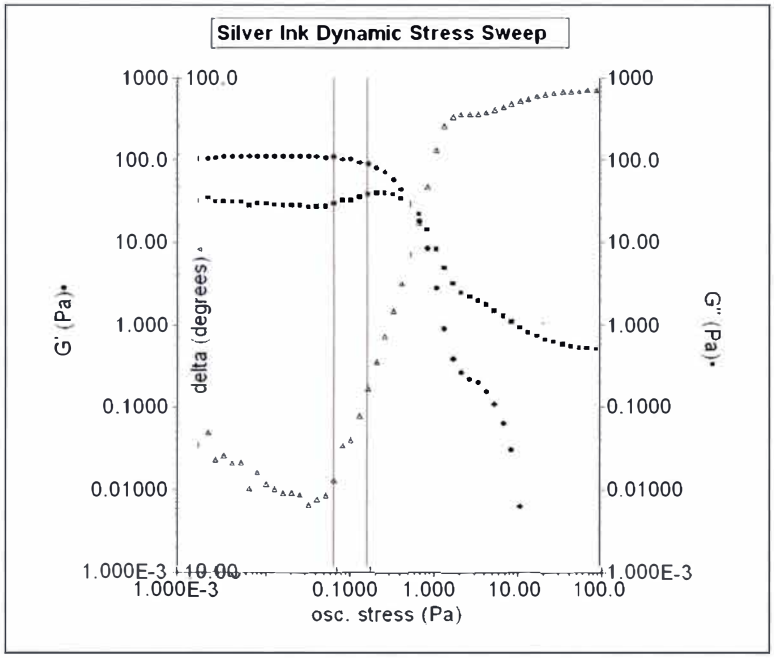

Figure 1: Silver-Flake Ink Dynamic Stress Sweep

A frequency sweep (Figure 2) was performed on the sample at the predetermined stress of 0.1 Pa. Here, the slope of the G' curve indicates the material's strength. A large slope reveals low strength, and a small slope indicates high strength. In this case, the G' curve remains fairly level until the frequency of 20 Hz is reached. At that point, G' drops off sharply. This result indicates that the ink maintains its strength until a frequency of 20 Hz, then the sample deforms quickly.

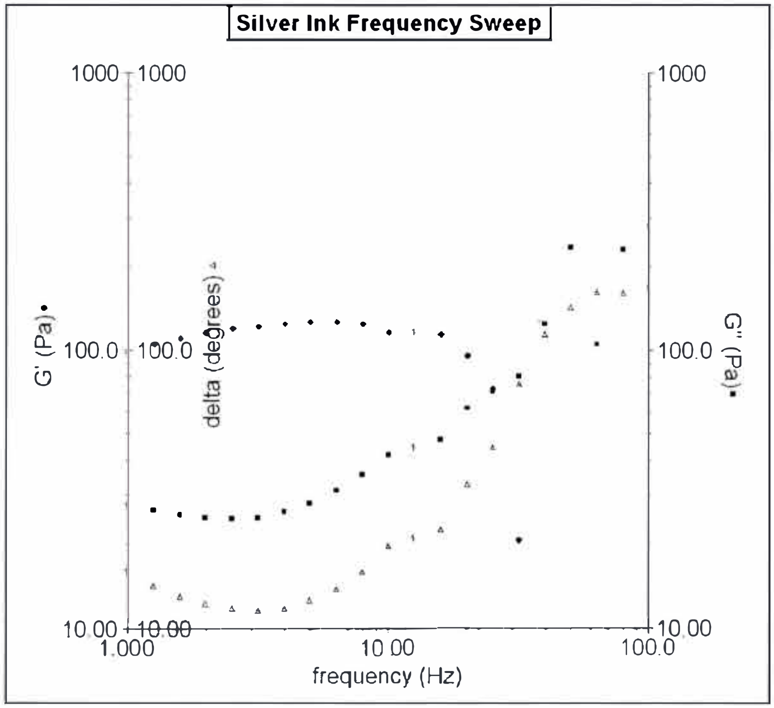

Figure 2: Silver-Flake Ink Frequency Sweep

The steady state flow test (Figure 3) was conducted to determine the critical stress of the ink. As in the dynamic stress sweep, a second plateau of stability can be seen in the steady state flow. The critical stress of the ink occurs at approximately 1 Pa.

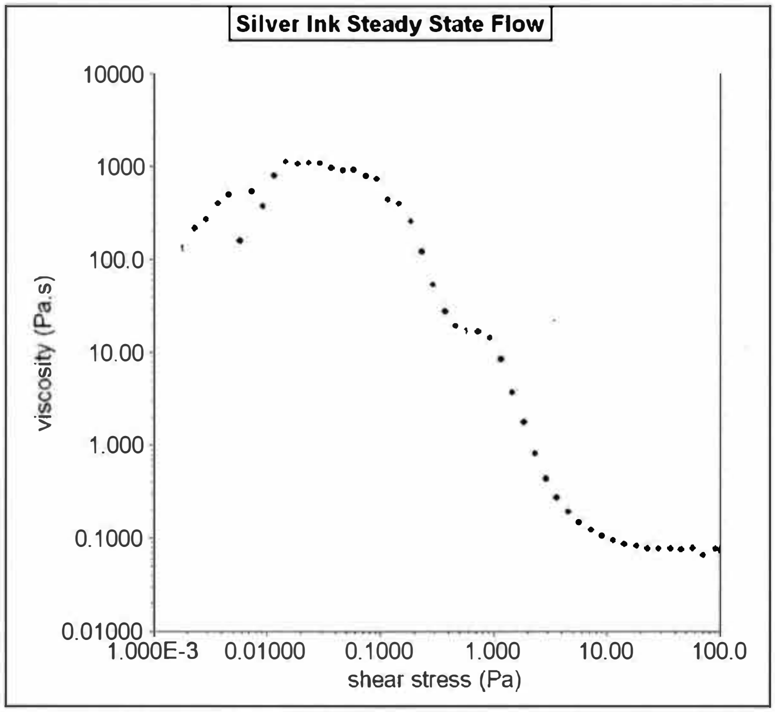

Figure 3: Silver-Flake Ink Steady State Flow

Substrates

The silver ink was hand-proofed onto five different paper substrates. Though each substrate was hand-proofed with ink in an identical manner, the thickness of the ink layer varied from substrate to substrate. The variations may be attributed to differences in ink holdout capabilities among the substrates, as well as a slight difference in manual force applied during application. These thicknesses were measured using a caliper and taken into consideration during the conductivity measurements. The LabelSet grade possessed the thinnest ink layer and the highest overall conductivity (Table 4).

Substrate	Length [cm]	Width [cm]	Thickness [cm]	Conductivity [S.cm^{-1}]
LabelSet	2	1.244	0.0003	2684
OptiTherm	2	1.239	0.0013	795
PointFlex	2	1.243	0.0005	2169
UniTherm	2	1.303	0.0009	1448
UniTherm Sharp	2	1.284	0.0010	1177

Table 4: Conductivity of Silver-Flake Ink on Tested Substrates

Ink-Substrate Interactions

Roughness

UniTherm Sharp was calendered to four roughness levels and hand-proofed with silver flake ink. Parker Print-Surf Roughness values were determined at a clamping pressure of 1000 kPa with a soft backing. The results for the different roughness values (Table 5) indicate that calendering has an overall detrimental effect on conductivity.

Calendering Conditions	Roughness [microns]	Thickness [cm]	Conductivity [S.cm^{-1}]
None	1.58	0.001	1177
10# 1 Pass 1 Side	1.31	0.001	945
40# 1 Pass Each Side	1.25	0.001	786
10# 2 Pass 1 Side	1.24	0.001	812
50# 3 Pass Each Side	1.15	0.001	852

Table 5: Effect of Surface Roughness on Conductivity

Though the thickness of the ink layer showed no relevant difference, the conductivity of the printed area generally decreases with a decrease in surface roughness. This trend is likely related to variations in the level of penetration of the ink into the substrate. Ink penetration into the paper was not quantified during this experiment, but it is recommended for future research.

Substrate Permeability and Porosity

The OptiTherm tag exhibited the highest permeability of the five substrates (Table 6). According to the mercury porosimeter results (Table 7), the PointFlex substrate has the highest percent porosity at 23.8%, closely followed by UniTherm Sharp at 23.1%. OptiTherm Tag displayed the lowest percentage at 18.6% porosity.

Sample	PPS Porosity [mL/min]	Permeability [μm^2]
LabelSet	1.65	5.74E-6
OptiTherm	5.74	5.13E-5
PointFlex	2.11	5.76E-6
UniTherm	2.23	8.03E-6
UniTherm Sharp	8.12	3.02E-5

Table 6: Parker-Print Porosity and Permeability of Substrates

	Intrusion Vol. [mL/g]	Total Pore Area [m^2/g]	Avg. Pore Diameter [A]	Porosity [%]
LabelSet	0.2273	0.184	49324	22.9
OptiTherm	0.2163	0.099	87662	18.6
PointFlex	0.2487	0.092	108210	23.8
UniTherm	0.2410	0.039	244925	21.8
UniTherm Sharp	0.2552	0.046	221776	23.1

Table 7: Mercury Porosimeter Data for Substrates

The porosity and permeability data for the substrates are compared to their final conductivity in Table 8 for easier comparison. The high permeability, low porosity sample exhibited a low conductivity; whereas the low permeability, high porosity substrate exhibited a high conductivity.

	Permeability [μm^2]	**Porosity [%]**	**Conductivity [S.cm^{-1}]**
LabelSet	5.74E-6	22.9	2684
OptiTherm	5.13E-5	18.6	795
PointFlex	5.76E-6	23.8	2169
UniTherm	8.03E-6	21.8	1448
UniTherm Sharp	3.02E-5	23.1	1177

Table 8: Relationship between Substrate Permeability, Porosity and Conductivity

Wetability

The contact angles of the silver ink with the substrates ranged from approximately 40 degrees (PointFlex) to 52 degrees (LabelSet). The high contact angle on the LabelSet sample correlates with its low permeability. However, the PointFlex sample exhibited a low contact angle despite its low permeability.

Substrate	**Contact Angle [deg]**
LabelSet SP	52.0
OptiTherm	46.5
PointFlex	39.9
UniTherm	45.4
UniTherm Sharp	48.0

Table 9: Contact Angles of Conducting Ink with Substrates

Relative Humidity and Temperature

An increase in the relative humidity of the sample's atmosphere at a given temperature resulted in a decrease in the conductivity of the printed area (Table 10).

However, once removed from the humidity chamber and exposed to ambient conditions, the printed substrate typically regained its original conductivity. Exceptions to this trend are seen at the high relative humidity conditions, where complete recoveries from the humid conditions were not accomplished. This is likely due to the physical warping that the samples experienced at high humidity levels. The decrease in conductivity at higher relative humidity levels may be related to the swelling of polymers present in the silver-flake ink. Polymer swelling would reduce contact area between the silver flakes, causing a decrease in conductivity.

Conditions		**Conductivity [S.cm^{-1}]**			
Temp [°C]	**Relative Humidity [%]**	**Avg.**	**Open 1**	**Open 2**	**Open 3**
23	35	1081	n/a	n/a	1323
23	50	1073	1035	1027	1028
23	80	761	n/a	1095	1087
23	90	767	806	814	820
30	35	1286	1340	1328	1332
30	50	1051	1373	1373	1373
30	80	918	704	714	704
35	80	1399	1299	1282	1299

Table 10: Effect of Relative Humidity on Conductivity

As seen in Table 11, an increase in temperature caused an increase in conductivity at the same relative humidity. As temperature increases, more moisture is present in the sheet at any given relative humidity. The relationship between temperature and relative humidity can be seen in Figure 4[39]. The increase in conductivity at elevated temperatures may be attributed to the thermal expansion of the silver flakes in the ink. This expansion would increase the contact area between the flakes, allowing for increased conductivity values.

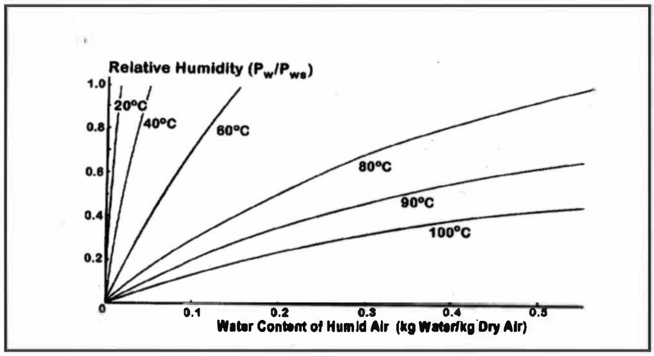

Figure 4: Relationship between Relative Humidity and Water Content of Air

Source: Peel, J., *Paper Science and Paper Manufacture*, Angus Wilde Publications, Vancouver, B.C., (1999), 53-54.

Temperature [°C]	**Relative Humidity [%]**	**Conductivity [$S.cm^{-1}$]**
23	35	1081
30	35	1286
23	50	1073
30	50	1051
23	80	761
30	80	918
35	80	1399

Table 11: Effect of Temperature on Conductivity

The effect of repeated increases and decreases in relative humidity at a constant temperature on conductivity was also investigated (Table 12). The initial increase in relative humidity caused a decrease in conductivity, as expected. The subsequent decrease in relative humidity caused the conductivity to drop further still. However, the second humidity increase resulted in a sudden increase in conductivity. The final humidity decrease again decreased the conductivity value. The reason for the spike in conductivity following the second humidity increase is unknown and should be further explored.

Run Number	Temperature [°C]	Relative Humidity [%]	Conductivity [$S.cm^{-1}$]
1	29	50	1484
2	29	85	1469
3	29	50	1370
4	29	85	1509
5	29	50	1423

Table 12: Effect of Repeated Humidity Change on Conductivity

CHAPTER VII

CONCLUSIONS

The research conducted in this work yielded some interesting phenomena. Decreased roughness caused a decrease in the conductivity of the printed sample. A substrate possessing high permeability and low porosity exhibited a lower conductivity than a substrate consisting of low permeability and high porosity. The contact angle of the silver-based ink did not show a strong correlation to the permeability of the substrate. Finally, an increase in relative humidity resulted in a decrease in conductivity, and an increase in temperature caused an increase in conductivity. The relative humidity results are likely linked to swelling of the polymers present in the ink. The temperature results are likely related to thermal expansion of the silver flakes in the ink, increasing contact points between the silver.

Paper substrate properties impose significant effects on the conductivity of printed electronics. Understanding these effects is a first step towards producing an ideal substrate to optimize printed electronic product performance. Future research should further explore the relationship between temperature, relative humidity and printed conductivity. If possible, several paper substrates should be produced in WMU's paper pilot plant and various coatings applied. Controlling both the substrate and coating characteristics will allow researchers to better understand the effects of various components on the final product.

REFERENCES

[1] Cohen, Beth, "Is RFID in Your Future?" http://networking.earthweb.com/nethub/article.php/10492_2216421_2

[2] "RFID Chips Are Here," http://www.theregister.co.uk/content/archive/31461.html

[3] Hoske, M. "RFID: Adoption Increases Despite Costs," Control Engineering, July 2004, pg. 46-47.

[4] Roberti, M. "Analysis: RFID – Wal-Mart's Network Effect," CIO Insight, 15 Sept 2003, http://www.cioinsight.com/article2/0,3959,1265594,00.asp

[5] Dunn, Darrell. "Defense Department Delays RFID Deadline Until At Least February," Compliance Pipeline 12 Nov 2004, http://www.compliancepipeline.com/52601247

[6] "RFID: Tomorrow's Active Packaging Technology" Paper, Film & Foil Converter 77 no8 AP3-AP4 Aug 2003.

[7] "RFID Chips Are Here" http://www.theregister.co.uk/content/archive/31461.html

[8] "Wal-Mart explains: 'Why RFID? Let me count the ways.'" Packaging Digest 40 no11 12 Nov 2003.

[9] Hoske, M. "RFID: Adoption Increases Despite Costs," Control Engineering, July 2004, pg. 46-47.

[10] Printed Electronics Review, "What are Printed Electronics?" Aug 2004, http://www.idtechex.com/printelecreview/en/article.asp?articleid=54.

[11] Zebra, "Electronic Product Code (EPC)" http://www.rfid.zebra.com/epc.htm

[12] Fildes, Jonathan. "Chips with Everything," *New Scientist* v. 176 (Oct. 19 2002) p. 45-7.

[13] "New Wireless Technology Promises Smarter Packages" Computerworld **34** no17 64 April 24 2000.

[14] Roberti, M. "Growing Low Cost RFID Antennas" RFID Journal 07 Jun 2004 http://www.rfidjournal.com/article/articleview/975/1/1/

[15] "Flint Ink Revolutionizes Antennas" RFID Journal http://www.rfidjournal.com/article/articleprint/41/-1/1

[16] "Packaging Poses Unique RFID Challenges" Chain Store Age 80 no5 sec2 38A My 2004

[17] Navas, D. "The Secret Life of RFID Antennas" 05 Nov 2004, downloadable at http://www.scs-mag.com/index.php?option=com_content&task=view&id=156&Itemid=90

[18] Wohlwend, M. "RFID: The Oncoming Wave" Catalog Success 6 no9 37-38, 40 S 2004

[19] "Retail's Biggest RFID Project" Chain Store Age 11A, 14A, 18A-19A O 2004 supp

[20] Reid, Keith. "The Barcode of the 21st Century" National Petroleum News 95 no10 36-8, 40, 42 S 2003

[21] Brewin, Bob. "Delta Says Radio Frequency ID Devices Pass First Bag-Tag Test" Computerworld 37 no51 7 D 22 2003

[22] "Brave New RFID World" Food Engineering 76 no1 81-2, 84, 87-8 Ja 2004

[23] "Tracking RFID progress" American Printer 232 no4 16-17 Ja 2004

[24] Pianoforte, Kerry. "The Specialty Ink Report" http://www.inkworldmagazine.com/Oct033.htm
[25] Hulme, G. and Claburn, T. "RFID's Security Challenge" InformationWeek 15 Nov 2004 http://www.informationweek.com/story/showArticle.jhtml?articleID=52601030&tid=13690
[26] RFID Concerns, http://www.rfidconcerns.com/
[27] TA Instruments, http://www.tainstruments.com/product.asp?n=1&id=35
[28] Joyce, Margaret, PAPR 640 Class PowerPoint Notes, Western Michigan University, Spring 2005.
[27] Adams, J., Faux, D., and Rieber, L. Printing Technology 4th edition, Delmer Publishers, Albany, NY, 1996.
[28] University of Houston, Graphic Technology, http://graphics.tech.uh.edu/MatProcesses/Flexography.html
[29] Printers' National Environmental Assistance Center, http://www.pneac.org/printprocesses/flexography/
[32] Fleming, Dan. IMAG 620 Class PowerPoint Notes, Western Michigan University, Fall 2005.
[33] Jennifer Rigney, "Materials and Processes for High Speed Printing for Electronic Components", *Proceedings of the IS&T NIP20: International Conference on Digital Printing Technologies*, Salt Lake City, 2004, pp275-278.
[34] Pal, L., Joyce, M. K. and Fleming, P. D., "A Simple Method for Calculation of Permeability Coefficient of Porous Media", *TAPPI advanced coating symposium*, February 8-10, 2006 in Turku, Finland
[35] Pal L., Joyce M. K., and Fleming P. D., "Pore Structure Parameters Properties - Effect on Barrier and Printing properties of Paper and Paperboard", 2005 Coating & Graphic Arts Conference & Exhibit, Toronto, April 17-20, 2005.
[36] Field, S., "Minimizing Flexo Ink 'Toning' Downtime DuringPressStartup"http://www.flintink.com/flintinkweb.nsf/GetWebGeneralLib/Minimizing+Startup+Downtime+Due+to+Toning?opendocument&subcat=GenLib.
[37] E. W. Washburn, Phys. Rev. Ser. 2, 17, 273 (1921).
[38] T555 om-99 "Roughness of Paper and Paperboard (Print-surf Method)", TAPPI (1999).
[39] Peel, J., *Paper Science and Paper Manufacture*, Angus Wilde Publications, Vancouver, B.C., (1999), 53-54.